

Nitrogen Bases and Carbon Deposits on Coal Liquefaction Catalysts

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Introduction

The respective roles of coke and alkali as poisons of coal liquefaction catalyst activity have attracted the interest of numerous researchers in the past decade (1-17). It is believed that coke formation occurs on catalyst acid sites and that the basicity of coke precursors is an important factor in determining the propensity for coke formation. It is also well-known that alkali metals, especially sodium, can poison acid sites. The coal liquefaction catalyst environment often contains basic compounds (nitrogen bases) and alkali metals (in the coal ash).

Recently, we have correlated elemental analysis data obtained for catalyst samples from the Wilsonville, Alabama coal liquefaction pilot plant. We were surprised to find that a simple mechanistic model involving (a) nitrogen bases chemisorbed on acid sites, and (b) poisoning of acid sites by sodium, can explain virtually all of the interesting coke-formation trends seen in the Wilsonville process since the inception of the two-stage liquefaction (TSL) process mode. The purpose of this paper is to describe this model.

Experimental

Catalyst samples used in this work were from the Wilsonville runs summarized in Table 1. Two catalysts are represented: Shell 324M NiMo/Al₂O₃ and Amocat 1C NiMo/Al₂O₃. Two coals are represented: Wyodak sub-bituminous and Illinois #6 bituminous. Four basic processing configurations are shown: Integrated Two-Stage Liquefaction (ITSL), Doubly Integrated Two-Stage Liquefaction (DITSL), Reconfigured Integrated Two-Stage Liquefaction (RITSL) and Close-Coupled Integrated Two-Stage Liquefaction (CCITSL). A more detailed description of these runs and process configurations can be found in reference (18) and in the Wilsonville run reports (19).

The important hydrotreater feedstream components in the model are represented by the three product streams from the critical solvent deashing unit, (CSD). The first, called the ash concentrate stream, contains coal ash and "resid" (defined as a vacuum non-distillate at 650 F and 0.1 mm Hg). The second, called the "thermal resid" (TR) stream, typically consists of resid and less than 10% distillate solvent; the third, called the "light thermal resid" (LTR) stream, typically consists of resid and 20-30% distillate solvent. Because of chemical and/or physical fractionation in the CSD unit, the resids in these streams are different: in terms of average molecular weight, one could expect "ash concentrate resid" > "TR resid" > "LTR resid". The streams also differ in resid concentration. For a given resid input to the CSD, the "TR resid" and "LTR resid" typically constitute about 40-50% each of the total, while the "ash concentrate resid" is usually less than 10% of the total. Thus the model does not

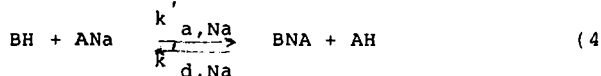
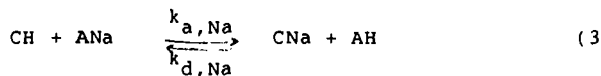
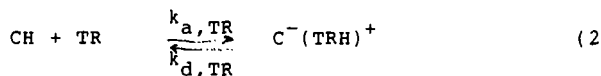
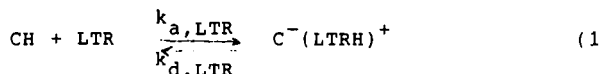
include a separate provision for "ash concentrate resid", but does provide for effects associated with the presence or absence of "TR resid", "LTR resid", and the coal ash in the ash concentrate stream.

Catalyst samples in process solvent were shipped from the Wilsonville pilot plant to our laboratory. THF-soluble material was removed from the catalysts using a Soxhlet extraction apparatus. Residual THF was desorbed in a vacuum oven overnight at ca. 120 C. Details of the elemental analyses can be found in reference (20). The total weight of deposited contaminants (C, H, N, Fe, Ti, Na and traces of Ca, V, K) was between 10 and 15% in all cases. Data are uncorrected for differences in weight basis.

Results and Discussion

Proposed Model

The following model, utilizing reactions involving basic nitrogen compounds, sodium, and acid sites, fits virtually all of the Wilsonville catalyst coking trends for runs 246 through 250:



where LTR represents nitrogen bases correlated with light thermal resid (or with distillate solvent), and TR represents nitrogen bases which correlate with thermal resid. CH represents an acid site that may react with either basic nitrogen or sodium, while BH represents a site that reacts with sodium alone. ANa represents sodium that is present in some ionic form in coal ash. $\text{C}^-(\text{LTRH})^+$ and $\text{C}^-(\text{TRH})^+$ represent the acid-base adducts, which are designated chemisorbed bases, and CNa and BNA represent the Na-exchanged acid sites, which are designated chemisorbed Na. Simplifying assumptions are that, on the average, base molecules contain only one nitrogen atom, and that saturation corresponds to one nitrogen atom per acid site. It is also assumed that CNa and BNA are not reactive towards nitrogen bases. In this model, the chemisorbed bases contain as much as 100% of the carbon on the catalyst at any time. The remainder of the carbon, if present, is assumed to be present as an essentially constant amount of non-nitrogen-containing process-derived coke.

The model, as written, is for Brønsted acid sites. However it can be written for combined Brønsted and Lewis acidity, or only Lewis acidity, with no loss of applicability. Of course, the

protonated nitrogen base must be held to the surface for Brönsted acidity to lead to carbon deposition by this model. Also, at this stage of development the model neglects condensation and/or hydrodenitrogenation (HDN) reactions of the chemisorbed nitrogen bases, since desorption of these bases is a key feature. The true coke formation mechanism is almost certainly more complicated than the model presented here.

Catalyst Characterization

Wyodak Coal, Shell 324M Catalyst. Figure 1 shows the %C, %N and %Na determinations for Shell 324M catalyst in Wilsonville runs using a Wyodak sub-bituminous coal. The series shown (246-DITSL, 246-ITSL and 249-RITSL) is especially interesting because a single catalyst charge was used for all three runs. The entire catalyst lifetime is thus depicted from left to right in Figure 1.

DITSL operation (LTR, no TR or ash) is characterized by essentially constant C and N levels during the operating period, and no Na accumulation. This represents a rapid saturation of acid sites by LTR-bases; the N level at saturation for this catalyst is about 0.7%.

On switching to the ITSL mode (LTR and TR, no ash) C increases, N remains constant, and Na does not accumulate. In our model, this corresponds to a gradual exchange of LTR-bases with TR-bases. Assuming that a pseudo-saturated surface exists during the exchange period, this requires that TR bases have a higher average molecular weight than the LTR bases. This is certainly consistent with the resids contained in the LTR and TR streams. Stohl and Stephens (8) published C analyses for the last month of 246-ITSL which clearly show the establishment of a new saturation level at ca. 10% C. This level, sketched in Figure 1, is consistent with the carbon level at the start of the 249-RITSL run period.

Finally, in the RITSL period, C and N decrease while Na increases. In fact, N decreases to essentially zero while at the same time Na shows evidence of reaching a saturation level. In our model this is due to a gradual exchange of nitrogen poisoned acid sites with Na-poisoned sites. It is clear that coal ash is the source of Na deposited on the catalyst.

Illinois #6 Coal, Shell 324M Catalyst. Figure 2 shows the characterization data for Shell 324M catalysts when Illinois #6 bituminous coal was used. Runs 248-DITSL and 248-ITSL represent a single batch of catalyst subjected to first DITSL, then ITSL, processing, but Run 247-RITSL was conducted with a separate catalyst batch. In this respect the data obtained with Illinois #6 coal feed are different than the Wyodak data in Figure 1.

DITSL data for Illinois #6 coal are virtually identical to that for Wyodak coal with a saturation level of ca. 0.7% N and 8% C. On switching to the ITSL mode, the C level increases with no change in N or Na, again consistent with an exchange of LTR-base with TR-base at pseudosaturated conditions. It is, as before, not clear if the exchange with TR-base has gone to completion at the end of Run 248-ITSL. However, it is obvious that the TR-bases derived from the Illinois #6 coal have a higher C/N ratio than TR-bases from the Wyodak coal because the C levels in 248-ITSL are higher than in 246-ITSL. Assuming an average of one N atom per base molecule, the average molecular weight of the Illinois #6 TR-

bases is 50% to 100% greater than that of the Wyodak TR-bases.

Run 247-RITSL data again show C and N decreasing as Na increases. In comparison to the Wyodak coal (Run 249-RITSL) data, more C is desorbed per desorbed N, again indicating Illinois #6 TR-bases have a higher average molecular weight than Wyodak TR-bases. Also, in comparison to Run 249, the N and Na levels at the end of Run 247 indicate that poisoning of acid sites had not reached completion when run 247 was terminated.

Since this RITSL catalyst was not previously subjected to the DITSL-ITSL exchange, the initial levels of C and N must correspond to a rapid saturation at startup; however, this saturation was not with LTR-bases, as occurs in DITSL mode. Instead, saturation occurs with the higher average molecular weight TR-bases. In contrast to organic base exchange, which is probably desorption-limited, adsorption on unsaturated sites should be rapid at process temperatures, and the rapid saturation with N indicates this to be the case. Stohl and Stephens (5) have shown that the presulfided Shell 324M catalyst will chemisorb N from a nitrogen-containing polycyclic aromatic coal liquid fraction rapidly enough to achieve saturation, reported by them to be 0.6% N, in two hours at 300 C. The initial C level in Run 247 shows reasonable agreement with the levels reached in 248-ITSL; this suggests the exchange of LTR and TR bases was near completion at the end of 248-ITSL.

Illinois #6 Coal, Amocat 1C Catalyst. The two periods of Run 250-CCITSL shown in Figure 3 used Illinois #6 coal and Amocat 1C NiMo/Al₂O₃ catalyst. These two periods are 250-CCITSL-NAR (no ash recycle) and 250-CCITSL-AR (ash recycle). They represent two separate batches of the Amocat 1C catalyst. Both batches indicate rapid initial saturation at ca. 12% C and 0.5% N, followed by a decrease in C and N levels and corresponding Na increase. The data taken in the ash-recycle period shows a more rapid increase in Na, and concurrent decrease in C, than the data for the no-ash-recycle period. This is most easily explained as a Na concentration effect, with the Na deposition rate increasing with sodium concentration in the reactor. The larger relative error in N determination makes the N trends less definite.

Elemental Correlations. Figure 4 shows plots of N versus C, normalized to moles per g catalyst, for all samples used in this study. Two distinct data clusters are immediately obvious: DITSL-ITSL data and RITSL-CCITSL data. All of the DITSL-ITSL data show essentially constant N content while for RITSL-CCITSL samples a direct relationship between C and N exists. The slope of the C-N data suggests stoichiometries for the desorbing bases. Trends show that the desorbing material is mainly coal-dependent: it has an average stoichiometry of about C₁₄N for Wyodak sub-bituminous coal, and about C₂₄N for Illinois #6 bituminous. These calculations are subject to the assumption that all of the net carbon loss is due to desorption of nitrogen bases. Also, the trends in the Amocat data are less well defined simply because the N-Na exchange is slower on this catalyst. Assuming that the initial coverage in all RITSL and CCITSL runs is essentially all TR base, then these average stoichiometries can be assigned to the TR bases.

Average stoichiometries for the bases chemisorbed on the catalyst when LTR and distillate derived from the Wyodak or Illinois #6 coals can be calculated from 246-ITSL and 248-ITSL

data; in the model this represents exchanges from essentially 100% LTR coverage to 100% TR coverage. Assuming the LTR- and TR-saturation points indicated by the surrounding DITSL and RITSL data in Figures 1 and 2, and using the $C_{14}N$ and $C_{22}N$ stoichiometries calculated for the appropriate TR bases, we next calculate an average stoichiometry for LTR bases derived from both coals of about C_8N , with no strong dependence on coal type. This number is less certain than the TR-base calculations as both TR-base numbers and the absolute %C numbers were required. Nevertheless, the numbers summarized in Table 3 represent our best estimate of the average stoichiometries of the nitrogen bases required to fit the characterization data to our model.

Figure 5 shows N plotted against Na, both in moles per g catalyst, for the RITSL and CCITSL data (DITSL and ITSL data show no Na uptake). The correlation here is good: all of the Shell 324M data fall on one line, and all of the Amocat 1C data falls on another. This relationship should reflect characteristics of the acid site populations of the two catalysts. For Shell 324M catalyst, three Na atoms are chemisorbed for each N atom desorbed; for Amocat 1C, two Na atoms are chemisorbed for each N atom desorbed. Assuming one N atom (or one Na atom) per CH site, and one Na atom per BH site, and assuming that all CH sites can react with Na (strongly suggested by the desorption of essentially all N in Run 249, for Shell 324 catalyst, but not strongly indicated for Amocat 1C, for which complete desorption of N was not seen) then two BH sites exist for every CH site on the Shell 324M catalyst, and one BH site for every CH site on the Amocat catalyst.

Laboratory Desorption of LTR-Bases

A key point in this model is the desorption of basic nitrogen compounds under coal liquefaction conditions. A laboratory experiment was performed recently in a 300 mL CSTR to duplicate the desorption of these bases indicated by the pilot plant data. A 100 g blend of various Wilsonville DITSL catalysts, still in the oil in which they were shipped, was placed in the reactor. THF was flowed over the catalyst bed at ca. 120 C until the oil was removed. This took approximately one week. Analysis of the catalyst at this point indicated about 0.45% N, which is somewhat lower than the saturation coverage of 0.7% N seen in the Wilsonville catalysts after THF Soxhlet extraction. As a separate check, a Wilsonville DITSL catalyst was Soxhlet extracted for almost 1000 hours and the %N level was found to remain constant. Temperature measurements indicated Soxhlet extraction occurs at about 65 C. It is possible that the CSTR extraction at 120 C causes bases to desorb that do not desorb in the Soxhlet apparatus.

After THF extraction in the CSTR, the feed was switched to tetralin at about 6 ml/hr and the temperature was increased to 350 C. H_2 was supplied only in makeup amounts, i.e. to enough to keep reactor pressure at about 2000 psi. The catalyst bed was gently stirred during the experiment. The reactor was cooled, and samples taken, twice weekly for the next month.

Results are shown in Figure 6. A significant loss of N, from 0.45% to a relatively stable 0.15% did occur during the run (figure 6b). The average stoichiometry calculated for the desorbing compounds (figure 6c), was $C_{30}N$, which is closer to TR-

base stoichiometry (estimated from process exchange) than the LTR-base stoichiometry. One possible explanation for the discrepancy could be the formation of non-nitrogen-containing coke on acid sites concurrent with nitrogen base exchange. Evidence for this was seen near the end of the CSTR experiment (figure 6a). Since only %C was used to estimate the LTR-base stoichiometry from the DITSL-ITSL exchanges, the C_8N figure could be low for this reason. Also, accumulation and loss of bases may be complicated than a simple adsorption/desorption process. A kinetic analysis of the nitrogen content based on a first-order desorption mechanism is shown in Figure 6d. The rate constant for desorption of N in this experiment, k_d, TR , is 0.04 day^{-1} , which is within a factor of four of rate constants calculated from the data for the spent catalysts from the Wilsonville runs. Thus the CSTR experiment is in qualitative agreement with the kinetic analysis of the spent Wilsonville catalyst data. Most importantly, the lab experiment confirms the reversibility of the N contained in the organic residue on the catalyst.

Conclusion

In this model, acid sites on the sulfided catalyst rapidly saturate with basic nitrogen compounds on start-up. These bases (called LTR-bases) are either in the LTR material, or in the distillate solvent. In turn these bases gradually exchange with nitrogen bases having a higher average molecular weight when the TR stream is introduced to the feed. This correlation does not necessarily imply any chemical difference in the two resids (LTR and TR), but may simply reflect an increase in the relative concentrations of distillate solvent and resid. On introduction of coal ash, the nitrogen-containing compounds desorb, and sodium is adsorbed on the catalyst. Coal dependence is seen in the TR-bases, with the Illinois #6 coal producing a higher average molecular weight deposit than the Wyodak coal; this is not seen for LTR-bases. Sodium adsorption demonstrates a catalyst dependence, indicating differences in acid site populations for the two Shell and Amocat catalysts.

Reversibility of the chemisorption of nitrogen bases has been demonstrated in our laboratory. Future experiments will concentrate on other key features of the model, such as base exchange and sodium poisoning.

Acknowledgement

This work was performed at the Kentucky Energy Cabinet Laboratory (KECL). The KECL is operated by the University of Louisville for the Kentucky Energy Cabinet.

Table 1.

Summary of Wilsonville Runs Correlated in This Work

<u>Run</u>	<u>Coal</u>	<u>Configuration</u>	<u>Catalyst</u>	<u>Comments</u>
246A	Wyodak	DITSL	Shell 324M NiMo	
246B	Wyodak	ITSL	Shell 324M NiMo	Started with catalyst from end of 246A
247	Illinois #6	RITSL	Shell 324M NiMo	
248A	Illinois #6	DITSL	Shell 324M NiMo	
248B	Illinois #6	ITSL	Shell 324M NiMo	
249	Wyodak	RITSL	Shell 324M NiMo	Started with catalyst from end of 246B
250-II	Illinois #6	CCITSL	Amocat ^R 1C NiMo	No ash recycle
250-III	Illinois #6	CCITSL	Amocat ^R 1C NiMo	With ash recycle

Table 2.

Hydrotreater Feed

	<u>TR Present?</u>	<u>LTR Present?</u>	<u>Coal Ash Present?</u>
DITSL	No	Yes	No
ITSL	Yes	Yes	No
RITSL	Yes	Yes	Yes
CCITSL	Yes	Yes	Yes

Table 3.

Best Estimate of Average Nitrogen Base Stoichiometry
Required to Fit Our Model to Wilsonville Catalyst Data

<u>Coal</u>	<u>LTR-Bases</u>	<u>TR-Bases</u>
Wyodak Sub-bituminous	C_8N	$C_{14}N$
Illinois #6 Bituminous	C_8N	$C_{22}N$
CSTR Laboratory Study	$C_{30}N$	

Figure Captions

- Figure 1. Elemental analyses for Shell 324M catalyst and Wyodak sub-bituminous coal.
- Figure 2. Elemental analyses for Shell 324M catalyst and Illinois bituminous coal.
- Figure 3. Elemental analyses for Amocat 1C catalyst and Illinois bituminous coal.
- Figure 4. C-N trends for all data.
- Figure 5. N-Na correlations for all data.
- Figure 6. Desorption of LTR-bases from Run 248 DITSL catalysts in CSTR at 350°C.

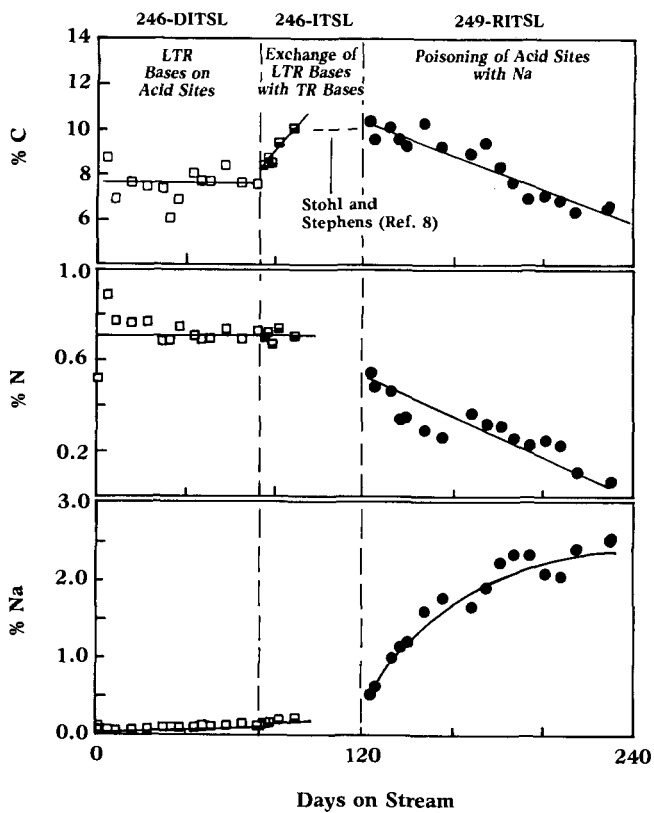
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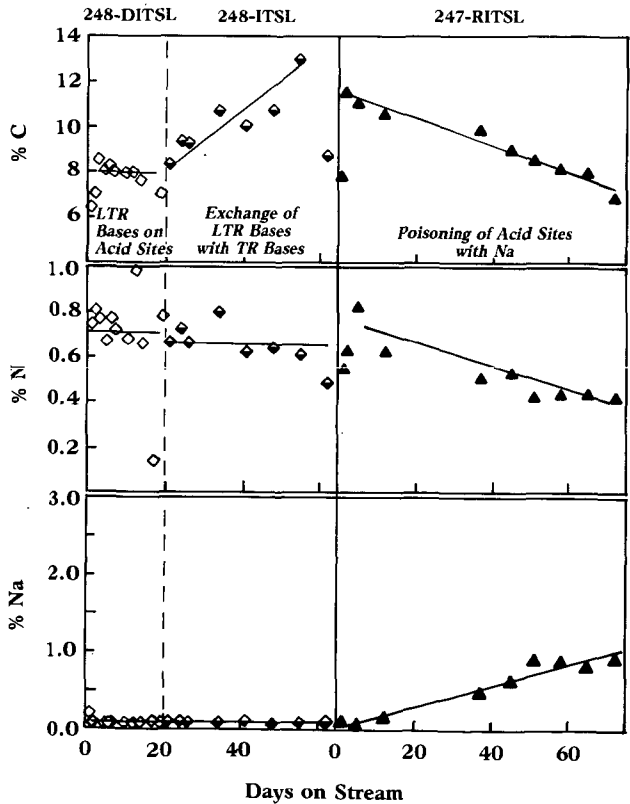
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Shell 324M Catalyst, Wyodak Coal



Shell 324M Catalyst, Illinois #6 Coal



Amocat® 1C Catalyst, Illinois #6 Coal

